SUMMARY

This thesis deals with the interrelation of the stable carbon and oxygen isotopes in the natural system: water - carbon dioxide - dissolved bicarbonate - solid carbonate.

A review is given of the fractionation factors for isotopic exchange equilibria between the compounds involved in the system mentioned above (chapter 1). Subsequently, the different procedures are described by which the various materials investigated are converted to carbon dioxide for mass spectrometric analysis (chapter 3). The isotopic results are corrected for different types of errors and reported on the internationally adopted PDB and SMOW scales (chapter 2).

In the second part (chapter 4) the isotopic composition of several kinds of natural waters is discussed. The seasonal variations in ^{18}O content of precipitation (fig. 4.2) and the relation between the ^{18}O content of average annual precipitation in Groningen and other European stations (fig. 4.3) are explained on the basis of the Rayleigh condensation model.

It is furthermore shown that rivers are also subject to seasonal variations, both in ^{13}C content of the dissolved bicarbonate and in ^{18}O content of the water. In winter all rivers have isotopic abundances of carbon and oxygen similar to those of the ground water in the drainage area. The higher ^{18}O content in rain water rivers during summer (fig. 4.5) is explained by the contribution of isotopically enriched precipitation, while the lower ^{18}O content of the melt water rivers from early spring onwards, is attributed to an isotopically light contribution from the Swiss mountains. The higher ^{13}C content of river water bicarbonate in summer (fig. 4.6) is considered to be due to isotopic exchange with atmospheric carbon dioxide of surface water draining into the rivers.

In the area investigated, ground water is found to have a rather constant and specific ^{18}O content; even when it is several thousand years old (table 4.1). This ^{18}O value is equal to that of the precipitation in the period of maximum infiltration, i.e. autumn and spring. Deviations are found to be due to admixture of sea water (fig. 4.4), or river water infiltration. The ^{13}C content of ground water bicarbonate shows a specific average value, which is explained by the dissolution mechanism of limestone in the soil by the action of carbon dioxide from humus decay and root respiration. Deviations from normal - caused by isotopic exchange with soil carbon dioxide, direct dissolution of limestone by humic acid or sea water infiltration - are observed and compared with some aspects of the chemical composition of the ground water (fig. 4.4).

The ^{18}O results for North Sea water agree with earlier measurements on the open ocean. The ^{13}C content of the sea water bicarbonate indicates a condition of carbon isotopic equilibrium with atmospheric carbon dioxide.

A gradual approach to isotopic equilibrium of fresh water bicarbonate with the carbon dioxide in the air is also observed in a shallow fresh water lake, the IJsselmeer (fig. 4.13).

Earlier measurements have shown that the ^{18}O content of brackish water is determined solely by the mixing ratio of the fresh and sea water components, as is the chlorinity (fig. 4.8). The same result is obtained for the carbon isotopes in the dissolved bicarbonate. On the basis of these findings, the relation between the ^{13}C and ^{18}O content in an estuary can be predicted, if the isotopic composition and the dissolved carbon content of the unmixed components are known (fig. 4.9).

The third part (chapter 5) of this thesis is concerned with the isotopic composition of shell carbonate precipitated in brackish water. The main aspects considered are: (a) the relation between the isotopic composition of shell carbonate and that of the surrounding water and (b) the significance of temperatures deduced from the ^{13}C and ^{18}O content of shells.

In the estuary of the Western Scheldt the respective variations in ^{13}C and ^{18}O contents of the shell carbonate and the water are found to correspond (fig. 5.3). If the δ^{13}-δ^{18} relation is extrapolated to marine conditions, the isotopic composition of carbonate precipitated in isotopic equilibrium with pure sea water can be deduced. The temperature derived from such an extrapolation, is a reasonable average for the growth period of the molluscs. The δ^{13}-δ^{18} relations of shells from other near-by estuaries reflect, when similarly extrapolated, the same temperature (fig. 5.4).

Hence it can be concluded that the molluscs: Mytilus edulis and Cardium edule, deposit carbonate in isotopic equilibrium with their environment, and that the difference in carbon and oxygen isotopic composition between carbonate on the one hand and water and dissolved bicarbonate on the other is determined solely by temperature.

From the ^{13}C and ^{18}O contents of the shell carbonate of young mussels collected during the course of one year on the Dutch North Sea coast (fig. 5.5), it is seen that only the extrapolation procedure applied to the δ^{13}-δ^{18} relation, yields reasonable temperatures for the growth period (fig. 5.6).

The procedure developed for determining the growth temperature of series of living molluscs can also be applied to fossil shells.